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A critical review of the development and demulsification processes applied for oil recovery from oil in water emulsions

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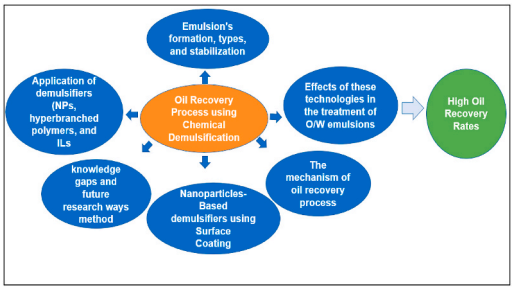
HIGHLIGHTS

- Oil in Water (O/W) emulsions formation, types, and stabilization were presented.
- An overview about the oil recovery process from O/W emulsions was discussed.
- The mechanism of oil recovery process using demulsifcation methods was reviewed.
- Chemical demulsifier showed promising results in recovering oil from O/W emulsions.
- Knowledge gaps and future research perspectives of chemical demulsification methods were discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation of stable emulsions is a fundamental problem in oil industry that can result in a sequence of environmental and operational problems. Chemical demulsification is extensively applied for the recovery of oil from water as well as water from oil. This review introduces different chemical demulsifiers applied for the demulsification and recovery of oil from oil in water (O/W) emulsions. Main types of surfactants (anionic, cationic, nonionics and amphoteric) involved in the formation of emulsions and enhances their stability were discussed. Promising demulsifiers such as nanoparticle (NP), hyperbranched polymers, and ionic liquids (IL), which achieved high oil recovery rate, parameters influencing demulsification efficiency and demulsification mechanisms were explored. Lastly, improvements, challenges, and new changes being made to chemical demulsifiers were underlined. Functionalized magnetic nanoparticles and hyperbranched polymers were very effective in recovering oil from O/W emulsions with an efficiency >95%. Polymers with highly hydrophilic content and high molecular weight can achieve excellent oil recovery rates due to higher interfacial activity, higher dispersion, and presence of specific functional groups. Although ionic liquids could achieve oil recovery up to 90%, high cost limits their applications. NPs showed excellent oil recovery behavior at low concentrations and ambient temperature. Demulsification efficiency of NPs can be enhanced by functionalize with other components (e.g., polymers and surfactants), while service life can be extend by silica coating. Future challenges include scaling up the use of NPs in oil recovery process and highlighting contrasts between lab-scale and field-scale applications.

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1. Introduction

In real systems, crude oil reservoirs are combined with gas and saline water. The presence of water dispersed in crude oil as a water-in-oil emulsion can cause different problems in crude oil production and transportation. When water is present in crude oil, problems with transportation are manifested by an increase in the viscosity of the produced fluids. The percentage of water in crude oil increase by increasing the pumping rate and the age of the reservoir (Jiménez et al., 2018) These unmixable fluids are emulsified by the simultaneous action of shear and pressure reduction at the head of the well, clogs, and controller valves (Matijasevic and Banhart, 2006). Emulsions are formed when at least two immiscible liquid phases are present within a system (Ali et al., 2021). The production of an emulsion mixture is comprised of a dispersed phase and a continuous phase (Goodarzi and Zendehboudi, 2019; Mohyaldinn et al., 2019). Emulsions are generally generated during oil production and recovery due to the use of chemicals with surface-active actions (Ali et al., 2020a). These chemicals reduce the interfacial tension between the two phases and help to stabilize the emulsion (Sjöblom et al., 2001). Similarly, the pH of the water phase helps to stabilize the emulsion (Sjöblom et al., 2001). The stability of O/W emulsions has been examined in several studies focusing on petroleum oil to create efficient and related methods for oil separation (Ali et al., 2020b).

Several problems occur in the transportation and treatment of crude oil due to the presence of the emulsion (Zolfaghari et al., 2016). These obstacles involve rising transportation costs, equipment, and pipelines corrosion as well as contaminating downstream refinery processes (e.g. catalysts) (Thompson et al., 1985). Thus, the O/W emulsion separation is a crucial method before the transportation and the treatment of crude oil (Hou et al., 2019). The most common demulsification processes are based on thermal, biological, electrical, chemical, and mechanical techniques (Peng et al., 2018; Wang et al., 2020). Between the aforementioned techniques, chemical demulsification is the highly commonly used method. The demulsification mechanism includes the use of chemicals that improve the film-thinning rate, reduce the stability of the emulsion and lead to oil separation from water. In this regards demulsifiers with great interfacial activity permeate into the interfacial film stabilized by the surfactants (Hou et al., 2012; Zargar et al., 2018), and the demulsifiers substitute the surfactants to break the interfacial film and increase the film drainage and hence enhance the oil recovery rates (Fan et al., 2010).

Demulsification processes applying different demulsifiers (Ali et al., 2019) have grown significantly due to the rapid development in oil and gas industries which generate vast quantities of oil (Matijasevic and Banhart, 2006). As such, the formation of emulsions is a complicated challenge facing the petroleum industry. Several demulsifiers such as polymeric surfactants, ionic liquids, and nanoparticles have been designed for the O/W separation (Shehzad et al., 2018). For example, silicon polyether (Zhai et al., 2020), ethylene oxide-propylene oxide (EO-PO) block copolymers (Niu et al., 2019), biodegradable polymeric surfactants (Feng et al., 2010), ionic liquids (Biniaz et al., 2016; Adewunmi and Kamal, 2019), magnetic nanoparticles (MNPs) (Chen et al., 2019) and non-magnetic nanoparticles (e.g. silicon oxide, titanium oxide and carbon-based materials (Hassanshahi et al., 2020; Ye et al., 2020). (Xu et al., 2019) have drawn significant interests in industrial fields. The amphiphilic materials with both hydrophilic and hydrophobic components are the highly popular demulsifiers. For example, hyperbranched polymers (Elmobarak et al., 2020; Elmobarak and Almomani, 2021c), Fe_3O_4 nanoparticles (Elmobarak and Almomani, 2021b), functionalized Fe_3O_4–SiO_2 nanoparticles (Elmobarak and Almomani, 2021a, Elmobarak and Almomani, 2021e) were successfully used to recover oil from O/W emulsions. These demulsifiers showed high oil recovery rates and demulsification efficiency up to 95%.

Strengthening oil recovery within the petroleum industry requires a commitment to developing demulsification mechanisms for O/W emulsions. As declared by (Kokal, 2005) oil is unlikely to be generated alone as it is typically formed with water, which produces numerous problems throughout the formation process. Moreover, oil production can be produced through two methods: first, the oil can be generated as free oil, which settles instantly; second, the presence of oil can result in emulsion production. Beyond that, the demulsification process is affected by numerous other parameters and factors, which are outlined below (Al-Sabagh et al., 2011; Zolfaghari et al., 2016; Yang et al., 2020):

- The addition of emulsifying agents (surfactant) at the O/W interfaces.
- The addition of different demulsifier materials to the emulsion mixture.
- The mixing time and rate (i.e., a long and high rate enhance the demulsification efficiency).
- The dispersion and mixing of these chemicals in the emulsion solution.
- The dispersion and mixing of oil inside the emulsion.

Based on the previous analysis, this review aims to identify and provide scientific literature on the knowledge gaps and future research ideas related to chemical demulsification methods for the recovery of oil recovery from O/W emulsions as well as the treatment for petroleum produced water. The review outlines the mechanisms of the demulsification process with respect to emulsion formation and types as well as the factors affecting emulsion stability. An overview of the oil recovery process from water emulsions using different chemical demulsifiers and the corresponding mechanism was presented and discussed. The application of different demulsifiers including magnetic nanoparticles (separately or coated), hyperbranched polymers and ionic liquids for oil recovery from O/W emulsions were explored. The review further analyzes the factors (size, concentration, salinity and wettability) that affect the demulsification efficiency and oil recovery process.

2. Methodology

This review provides an overview of the findings from recent studies between 2016 and 2021 that have applied the chemical demulsification process to recover oil from O/W emulsions. Some important articles published between 2000 and 2015 were also considered as they presented crucial data. Approximately 200 articles were searched from Google-scholar and Scopus databases, 168 relevant articles were kept, and 32 were discarded. The keywords searched were “enhanced oil recovery,” “O/W emulsion,” “demulsification method,” “nanoparticles,” “hyperbranched polymers,” “ionic liquid,” and “review.” The assembled data are introduced in Tables 1–5 and studied in seven sections. First, the surfactant types of stabilizing emulsions and the primary technologies used for the enhanced oil recovery process are presented in Tables 1 and 2. Abd they were discussed in Section 3 and Section 6, respectively.

Finally, the application of the demulsification method in the oil recovery process using different demulsifiers including NP, hyperbranched polymers, and ionic liquids, are reviewed in Section 8 and Tables 3, 4 and 6, respectively. Conversely, Table 5 presents the common anions present in the ionic liquid. Information about the emulsion formation, types, stability, and the impact of the surfactant on the emulsion interfacial films is discussed in Section 3, with an overview of different types of emulsions presented in Fig. 1. The classification of the surfactant and the structure of the surfactant molecule are shown in Fig. 2 and Fig. 3, respectively. The mechanism for the chemical demulsification method is examined in Section 6, and Fig. 4 represents the overall demulsification mechanism. Fig. 5 presents the number of technical articles published on the application of nanoparticles for the oil recovery process. Fig. 6 shows a representative image of the application of Fe_3O_4–SiO_2 hybrid nanocomposite in the demulsification of O/W emulsions.

Fig. 7 exemplifies the magnetization of nanoparticles in the absence

of a magnetic field as well as with the presence of a strong magnetic field. The hyperbranched polyglycerol polymers (HPG) structure is shown in Fig. 8 (Section 8.5). The structure of the common ionic liquids cations is presented in Fig. 9. Also, the application of some ILs types, including the HIL and Non-HIL ionic liquids, was represented in Fig. 10. Lastly, from the data analysis, challenges moving forward and recommendations for additional research are outlined.

3. Emulsions

An emulsion is formed when two or more non-mixable liquids combine to produce a continuous and dispersed phase. Typically, the phase with the lesser amount is the dispersed phase, and the phase with the greater amount is the continuous phase. However, suppose the amount in the two phases is similar. In that case, other parameters can be used for the classification of the continuous and dispersed phases (Kokal, 2005; Goodarzi and Zendehboudi, 2019). According to the Bancroft theory, a continuous phase is when the emulsifying agents are more solvable (Bancroft, 2002) Principally, emulsions have an oil phase and a water phase. Small particles, crude oils, and surface-active composites such as SARA (saturates, asphaltenes, resins, and aromatics) act as natural surfactants (i.e., emulsifying agents) (Wong et al., 2015; Abdulredha et al., 2020). Beyond strongly mixing, natural emulsifying agents can adsorb at the interface of oil/water, forming a solid interfacial thin layer over the dissolved drops and obstructing the coalescence of the droplets (Grenoble and Trabelsi, 2018). The tension between the oil and water phases is known as interfacial tension (IFT). A high IFT correspondingly leads to a high steady emulsion (Kumar and Mandal, 2018).

Following the dispersed phase, emulsions are classified as oil in water (O/W), water in oil (W/O), or multiple emulsions as water in oil in water (W/O/W) or oil in water in oil (O/W/O) as reported by (Prichapan and Klinkesorn, 2014) (see Fig. 1). Oil in water emulsions occur when oil drops are in the dispersed phase (i.e., internal phase) in the continuous water phase (i.e., external phase), also called a reversal emulsion. The production of W/O emulsions occurs when the drops of water are in the dispersed phase in the oil phase (i.e., continuous phase). However, multiple types are a combination of oil in water and water in oil emulsions. When oil drops are in the dispersed phase in water particles,

Table 2
The primary types of existing technologies for the enhanced oil recovery process, mechanisms, and challenges.

Oil recovery methods	Detailed procedures	Mechanisms	Challenges	Reference
Thermal methods	Steam flooding Cyclic steam stimulation (CSS) In-situ combustion Electrical heating	Decrease in the viscosity Decrease in the IFT Steam distillation Oil expansion Gravity discharge	High cost Low thermal conductivity Heat leak to the unsought films Low effective thermal degradation Heat deficiency from heat producer to the reservoir	(Kong and Ohadi, 2010; Viebahn et al., 2015)
Chemical methods	Alkaline flooding Surfactant flooding Polymer flooding Micellar flooding	Decrease in the IFT Wettability alteration Movement management Emulsification	The high cost (additional quantity required) Low efficiency on IFT and viscosity alterations Damage owing to inconsistency Un preferable movement ratio Sluggish dispersion rate	(Kong and Ohadi, 2010; Viebahn et al., 2015)
Gas methods	Injection of hydrocarbon gas Injection of CO_2 Injection of N_2 Injection of water alternating gas (WAG)	Decrease in the viscosity Oil expansion Pressure maintenance Miscibility	Gravity override CO_2 corrosion Miscible flooding requires minimum miscible pressure (MMP) Early gas permeation	(Kong and Ohadi, 2010; Viebahn et al., 2015)

Table 1
Information and examples about the four types of surfactants.

Surfactant types	Definition	Examples	Charge carrier	Reference
Anionic	Surfactants that are dissociated in water into an amphiphilic anion and a cation, usually alkaline metal (Na+, K+) or quaternary ammonium	Phosphate esters, Sarcosine, Stearine/Stearic fatty acids. Sodium lauryl sulfate Sodium dodecylbenzene sulphonate (SDBS) Sodium lauroyl sarcosinate (INCI)	Negative	Kume et al. (2008)
Cationic	Surfactants are dissociated in water into an amphiphilic cation and an anion, most frequently halogen type.	Benzalkonium, Benzethonium, Methyl benzethonium, Cetylpyridinium, Alkyl-dimethyl Dichlorobenzene Ammonium, Dequalinium, Phenamylinium, Chlorides, Cetrimonium, Cethexonium bromides	Positive	Kamal et al. (2017b)
Nonionic	Surfactants that have multiple polar groups in their hydrophilic end are typically not as effective as ionic surfactants and are frequently used in combination with ionic surfactants	Polyglycerol alkyl ethers, Glucosyl dialkyl ethers, Crown ethers, Ester-linked surfactants, Polyoxyethylene alkyl ethers, Spans (sorbitan esters) and Tweens (Polysorbates).	No electrical charge	(Shahi and Bhattarai, 2018)
Amphoteric (Zwitterionic)	Surfactant molecules display both anionic and cationic dissociations.	Phospholipids Alkyl betaines, alkyl dimethyl imidazoline derivatives such as alkyl amphoacetates	Positive and negative charges (dependent on emulsion pH)	Shamsuri (2020)

subsequently dispersed in the continuous oil phase, the oil in water in oil emulsion is created. Conversely, water in oil in water emulsions are created vice versa. The presence of various emulsions is widespread in food, cosmetics, pharmaceutical industries, and wastewater treatment (Abullah et al., 2016; Kovács et al., 2016). However, these emulsions are kinetically stable but thermodynamically unsteady as they are generated from a mix of two or more unmixable liquids, which requires later separation. Nonetheless, the kinetic stability of the emulsion suggests that emulsions are steady for extended periods (days to a week) due to the creation of strong films over them via emulsifiers (Zolfaghari et al., 2016). Dependent upon the time that one phase can remain dissolved in the other phase, the emulsions mentioned above can be classified into stable, monostable, entrained water, and unstable (Fingas and Fieldhouse, 2004; Abdulredha et al., 2020). Typically, steady water in oil emulsions holds the majority of the water in the oil phase for more than 5 days (de Folter et al., 2012). Conversely, monostable emulsions are steady for 1–3 days. Further, entrained water and changeable W/O emulsions are not considered steady emulsions as both may stay in the water in oil for fewer than 1 day (Fingas and Fieldhouse, 2004; Raya et al., 2020).

The emulsion type is crucial for choosing demulsifiers solvable in the continuous phase and can reach the interface (oil/water interface) (Abullah et al., 2016). The type of emulsion is reliant upon the attraction of surfactants to the water or oil phase. If the surfactant has an affinity to the oil phase (i.e., hydrophobic surfactants), water/oil emulsions can be produced, though the hydrophilic surfactants would generate oil/water emulsions. Natural surfactants have a similar tendency as the oil and water phases, resulting in unstable emulsions. Moreover, the parameters defining the surfactant's attraction have a relative solubility number (RSN), hydrophilic-lipophilic deviation (HLD), hydrophilic-lipophilic balance (HLB), and recovery (R_{oil}) ratio (Wu et al., 2003, 2004). A high affinity of surfactants to a hydrophilic or lipophilic phase leads to the creation of fewer steady emulsions as the surfactants are likely to remain in the emulsion instead of transferring to the interface of oil and water (Borges et al., 2009).

Emulsion stability is linked to the type and volume of the surfactants. The surfactants encourage emulsion stability by creating a film over the water droplets in the O/W interface. The production of films enhances the emulsion stability by raising the interfacial viscosity and reducing the IFT (Sun and Armstrong, 2010). Further, factors such as oil concentration and mixing rate can alter the stability of the emulsion (Kunz and Häckl, 2016). By injecting energy into the system, the particles will break down into smaller sizes, eventually becoming emulsions. The physical features of the O/W interfacial films can be affected by the parameters mentioned above. In contrast, the surfactant solubility in the oil and water phase can affect the emulsion stability (Langevin et al., 2004). Moreover, emulsions are thermodynamically unstable, and the characteristics of the emulsions vary at different times. As such, to understand the mechanism of emulsion stability, it is crucial to examine the emulsion's thermodynamic and kinetic stabilities.

Generated oilfield emulsions are steadied with films that create over the water droplets at the O/W interface (Zolfaghari et al., 2016). The films result from the high-molecular-weight polar particles adsorption that is interfacially active (i.e., surfactant-like performance). The films

Table 3
Different nanoparticle types were applied separately and added to other materials for the oil recovery process.

NP type	NP Amount (wt %, mg/L)	Additive materials	Oil recovery rate (R_{oil}%)	Results and Comments	Reference
SiO_2	1 wt%	Polyacrylamide	90%	Increased the emulsion viscosity and the emulsion stability after polymer addition	Jafarnezhad et al. (2017)
SiO_2, $Fe(OH)_3$, TiO_2, Al_2O_3	0.2 wt%	Xanthan gum	80–89%	Improved the emulsion viscosity	Corredor et al. (2019)
Al_2O_3	0.05 wt%	Anionic surfactant	88.5%	Wettability alteration of the emulsion to oil-wet.	Betancur et al. (2019)
SiO_2	0.01–3 wt%	–	81–89	Improved oil and nanoparticles dispersion in the emulsion mixture	El-Diasty and Aly (2015)
ZrO_2	0.1 wt%	Cetrimonium bromide surfactant	40%	Change the emulsion mixture wettability to oil-wet.	Kamal et al. (2017a)
Pyroxene	1 wt%	–	89.5%	Decreased the IFT and changed the contact angle between the oil and water phases	Kamal et al. (2017a)
CeO_2, ZrO_2, Al_2O_3, TiO_2, MgO, $CaCO_3$, SiO_2	5 wt%	–	91–92%	Enhancement in the emulsion mixture viscosity	Nazari Moghaddam et al. (2015)
TiO_2	2–2.6 wt%	Sodium dodecyl sulfate surfactant	96%	Enhanced rheological characteristics	Shi et al. (2016)
SnO_2	2 wt%	–	78%	Reduction in IFT and wettability alteration of O/W emulsion	Jafarnezhad et al. (2017)
ZnO	1.6 wt%	–	89%	Reduction in IFT and emulsion viscosity	Ogolo et al. (2012)
SiO_2	0.31 wt%	Xanthan gum polymer-surfactant	73%	Increased the oil viscosity in the emulsion	Saha et al. (2018)
SiO_2, TiO_2, Al_2O_3	0.1–0.4 wt%	HPAM	93%	Development in the rheological characteristics	Corredor et al. (2019)
Nickel	0.005–0.02 wt %	Xanthan gum	94%	High emulsion viscosity	(Guo et al., 2017, 2018)
SiO_2	1 wt%	Polyethylene glycol	92%	High rheological properties	(Sharma et al., 2016; Sharma and Sangwai, 2017)
Fe_3O_4	1 wt%	–	35% Enhancement in oil recovery	Reduction in IFT and crude oil recovery.	(Guo et al., 2017, 2018)
Fe_3O_4	10 mg/L	SiO_2	93%–94.3%	An excellent oil recovery rate (R_{oil} < 90%) was achieved at high oil concentration (C_{oil} < 2000 mg/L) using MNPs doses ≤10 mg/L.	(Elmobarak and Almomani, 2021a, e)
Fe_3O_4	10 mg/L	SiO_2 with different thicknesses in the range (5–15 nm)	87.5%–96.3%	The MNPs exhibited excellent oil recovery and high magnetization values (46.1 and 80.2 emu/g). Adding 5,8,10, and 15 nm silica layers on the Fe_3O_4 MNPs preserved them from oxidation, expanded their service life, and attained R_{oil} ≥96.3%.	Elmobarak and Almomani (2021d)
Fe_3O_4	10 mg/L	–	≥98%	The Fe_3O_4 has achieved R_{oil} ≥ 98% for C_{oil} in the range of 200–800 mg/L utilizing MNPs ≤10 mg/L.	Elmobarak and Almomani (2021b)

Table 4
The application of hyperbranched polymers in the oil recovery process.

Polymer type	Results and Comments	Reference
Triblock copolymers	Polymers with lengthy hydrophobic bonds were noted efficient for W/O and O/W emulsions, while polymers with shorter hydrophobic bonds are efficient for the demulsification process	Le Follotec et al. (2010)
Polyether copolymers dependent on polyethyleneimine (PEI)	The demulsification ability is enhanced by expanding the size of the hydrophobic units of the polymers	Wang et al. (2015a)
PEO-PPO (diblock) polyether	The demulsification process can be attained at an extremely small concentration (as low as 1 wt%)	Pensini et al. (2014)
Polyacrylamide	Enhancement in the demulsification process and the polymer regenerated up to 20% extra oil	Abidin et al. (2012)
Hydrolyzed Polyacrylamide (HPAM)	Effective enhancing O/W emulsions stability but at the same time complicate the water treatment process	Li et al. (2007)
	The stability of emulsions was developed, HPAM can adsorb at the O/W interface between the oil phase (oleic) and water with no reduction in the IFT. Improving the concentration of HPAM polymer results in an increase in the Zeta potential, and emulsion stability	
Hydrolyzed Polyacrylamide (HPAM)	The O/W emulsion stability was enhanced with the polymer by steric and electrostatic stabilization.	Li et al. (2007) Li et al. (2007)
	Oil recovery was enhanced, but a strongly steadied O/W emulsion complemented the generated oil	
Dendritic polymer “broom molecule polymer.”	Excellent demulsification behavior versus an O/W emulsion and high recovery	Wang et al. (2008)
PEO/PPO-based copolymers	PEO/PPO-based copolymers were found to be less efficient than star polymer that relied on ((nitrilotris (ethane-2,1-diyl)) tris (oxy)) tris (4-oxobut-2-enoicd) for crude O/W emulsions treatment	El-Sharaky et al. (2019)
Benzyl-G3 and octyl-G3 hyperbranched demulsifiers	Great demulsification efficiency for the O/W emulsion	Bi et al. (2017)
Amine-based dendrimer polyamidoamine (PAMAM)	Attained a demulsification rate of 96.66% for a diesel/water emulsion using low demulsifier volume and low temperature in a short time	Hao et al. (2016)
Amine-based dendrimer demulsifier PAMAM (polyamidoamine)	The polymers had a great demulsification efficiency in a diesel O/W emulsion and produced very fine oil particles	Yao et al. (2014)
Hyperbranched poly (amidoamine) (h-PAMAM)	The demulsifier with 1,3-malonediamine as the dominant core had greater demulsification effectiveness for a diesel/water emulsion in comparison to the demulsifier that has ethylenediamine core	Zhang et al. (2018)
Hyperbranched poly (amidoamine) (h-PAMAM) using 1,4-phenylene diamine (PPDA)	High separation the diesel/water emulsion at high temperature (60 °C) even low demulsifier dose	Kuang et al. (2020)
Hyperbranched polyglycerol polymers (HPG)	The HPG with hydrophobic and hydrophilic features are capable of abiding by the O/W interface, decreasing IFT and adsorption time and enhance oil separation rate up to 90.3% via improved flocculation and coalescence method.	Elmobarak et al. (2020)

Table 5
Common ionic liquids anions(Bin Dahbag et al., 2016; Ren et al., 2020).

Anions	Abbreviation	Types (organic/inorganic)
Chloride	Cl^-	Inorganic
Bromide	Br^-	Inorganic
Fluoride	F-	Inorganic
Methane sulfonate	$R_3C–S–O_3^-$	Organic
Alkyl sulfate	$R\text{-}O\text{-}SO_3^-$	Organic
Hexafluorophosphate	PF_6	Inorganic
Tetrafluoroborate	BF_4	Inorganic
Iodide	I^-	Inorganic
Bis (trifluoromethyl sulfonyl) imide	$[(CF_3SO_2)_2N]^-$	Inorganic

improve the emulsion stability by (a) decreasing the IFT and (b) raising the interfacial viscosity. However, highly viscous interfacial films hinder the oil/film discharge rate through the coagulation of the water particles by providing a mechanical barrier to coalescence. This can result in a reduced rate of emulsion separation (Kumar and Mandal, 2018). However, a greater correlation occurs between the rate of incompressible interfacial film and emulsion stability. These films are classified into two types according to their movements. Additionally, the properties of interfacial films are a function of the type of crude oil, the composition of oil, the water pH, the degree to which the adsorbed film is driven, contact or aging time, and volume of the polar particles in the crude oil (Saththasivam et al., 2016; Luo et al., 2019).

The term surfactant is an acronym for surface-active agents, which have two primary characteristics: hydrophilicity and hydrophobicity. These two characteristics indicate the surface-active nature of the types of composites and their property to adsorb at interfaces. The polar part demonstrates a powerful attraction for polar solvents and is often hydrophilic or hydrophile. The polar part, hydrophobic or lipophile, has an attraction for oil (Fig. 2) (Raffa et al., 2015).

To prepare kinetically stable emulsions, an emulsifier (surfactant) is required to retain the freshly produced droplets compared to destabilization methods. The surfactant generates a protecting interfacial film when it adsorbs onto the surface of the droplets, inhibiting the particles from combining. Moreover, the surfactant typically keeps the physical and chemical condition of the emulsion by acting as a thickening agent to improve the viscosity of the water phase, which subsequently reduces the droplet encounters and the precipitation rate (Borreani et al., 2019). The demulsifier hydrophilic-lipophilic balance (HLB) is an essential component that indicates the comparative concurrent attractiveness of the oil or water phase. A range between 0 and 20 is used to describe the nature of the surfactant. HLB values greater than 10 (a high HLB value) indicate that the surfactant is hydrophilic and appeals to the water phase, producing O/W emulsions.

In contrast, an HLB value smaller than 10 (a low HLB value) suggests that the surfactant is attracted to the oil phase, producing W/O emulsions. However, when the HLB value equals 10 the oil and water-attractive groups are stable (Ojinnaka et al., 2016). As such, surfactants are categorized into four broad types: anionic (Kume et al., 2008) cationic (Kamal et al., 2017b) nonionic (Shahi and Bhattarai, 2018) amphoteric (Shamsuri, 2020), and (Fig. 3) (Hodges et al., 2019) See Table 1 for information about the types of surfactants used for stabilizing oil in water emulsions.

4. Surface wettability

Wettability is one of the highly significant surface properties that impact the use of the material, in the fields of enhanced oil recovery (EOR) (Al-Yaseri and Jha, 2021; Zivar et al., 2021). The contact angle formed between the surface and liquid phase is usually used for describing the wettability behavior. Various techniques and measurements have been used for the determination of the wetting characteristic of material surface (Lazghab et al., 2005). Commonly, superhydrophobicity, hydrophobicity, hydrophilicity, and super hydrophilicity have been categorized as a wettability index. In such categories, the contact angle for superhydrophobicity the static water contact angle is $> 150^{\circ}$ and very low contact angle hysteresis $<5^{\circ}$, while the static water contact angle is $> 90^{\circ}$, $<90^{\circ}$, and $<60^{\circ}$ for hydrophobicity, hydrophilicity, and super hydrophilicity, respectively (Sam et al., 2019; Zhang et al., 2020). Different studies evaluated the wettability of O/W emulsions using ionic surfactants as demulsifiers for oil removal (Wang et al., 2011; Afekare and Radonjic, 2017). When the ionic surfactants are introduced into the O/W surface, the wetting region of the surface might turn to water/wet because of the desorption of oil. Still, when the surfactants are placed in the undefiled charged surface, the hydrophobic phase is created onto the surface via interactions, causing the lyophobic wettability (De Oliveira et al., 2020). The wettability can be altered with an increase in temperature. A surface with high wettability can be produced by rolling and coating techniques (Shi et al., 2016). Depending on these varying approaches, hydrophobic and/or hydrophilic alteration can be applied to perform various functions in produced water treatment and oil recovery.

The hydrophilic surface alteration is highly significant in enhancing oil recovery and can be achieved by the addition of inorganic ions and certain surfactants with hydrophilic head groups [4,20]. After primary and secondary oil generation, the remaining oil creates a hydrophobic surface on the rock, which disrupts the oil separation. Thus, the wettability alteration encourages the separation of the remaining oil from the reservoir surface and plays a role as the main mechanism in the oil recovery technique (Jarrahian et al., 2012). Numerous oil replacement techniques such as surfactant flooding (SF), molecule deposition (MD), low salinity water flooding (LSWF), filming flooding (FF), and

Table 6
Recent application of ionic liquids as demulsifiers in oil recovery from O/W emulsion.

Ionic liquids	Cation Type	Anion Type	Emulsion Type	Dosage (ppm)\	Oil Recovery (%)	Result and Comments	Reference
$C_n$mim NTf_2 n = 10,12,14	Imidazolium	bis (trifluoromethyl sulfonyl)imide	O/W	100–3500	90–93.6	Increasing the concentration of ILs or the portion of hydrophobic alkyl cation chain enhanced the demulsification efficiency.	Hazrati et al. (2018)
$C_n$mim PF_6 n = 10,12,14	Imidazolium	Hexafluorophosphate	O/W	500–3500	71.2–86.2	For hydrophilic ILs, increasing the concentration of ILs or the length of the alkyl cation chain of ILs resulted in aggregation and decreased the demulsification efficiency.	Hazrati et al. (2018)
C_{12}mim NTf_2	Imidazolium	bis (trifluoromethyl sulfonyl)imide	O/W	5–125	30–70	The application of long alkyl chain lengths ILs (12 carbon atoms) was further efficient to replace the surfactants, which improved the IFT and decreased the $\%R_{oil}$.	Alves et al. (2017)
TOMAC	Ammonium	Chloride	O/W	1000–2000	95.1–100	Increasing ILs concentration to 1040 ppm at pH of 7 increases the $\%R_{oil}$. TOMAC achieved 100% (100%) due to the presence of hydrophobic chains.	(Biniaz et al., 2016; Adewunmi and Kamal, 2019)
TOMAB	Ammonium	Bromide	O/W	1000–2000	65	Increasing ILs concentration 1485 ppm at temperature 80 °C enhances the $\%R_{oil}$. from 30% to 65%.	(Biniaz et al., 2016; Hassanshahi et al., 2020)
CTAB	Ammonium	Bromide	O/W	300–800	90.3	Increasing ILs concentration to 333 ppm at 80 °C achieved 90.3% demulsification efficiency	Nandwani et al. (2017)
$P_{666,14}$ NTf_2	Phosphonium	bis (trifluoromethyl sulfonyl)imide	O/W	–	<95	Steady emulsions are present in the system with $P_{666,14}$ NTf_2 ILs due to absence of surface-active area in hydrophobic ILs.	Pillai et al. (2018)
$P_{666,14}$ Phos	Phosphonium	Dicyanamide	O/W	–	<90	No change in emulsions in the presence of $P_{666,14}$ [Phos] ILs ionic liquids due to absence of surface-active area in hydrophobic.	(Bin Dahbag et al., 2016; Ren et al., 2020)
$P_{666,14}$ Cl	Phosphonium	Chloride	O/W	–	<90	Halogenide ionic liquids (HILs) such as $P_{666,14}$ [Cl] removed oil from water in short period (≤20 min) compared to non-halogenide ionic liquid (Non-HILs) like $P_{666,14}$ $[N(CN)_2]$) (24 h).	(Bin Dahbag et al., 2016; Ren et al., 2020)
$P_{666,14}$ Br	Phosphonium	Bromide	O/W	–	<90	HILs (e.g $P_{666,14}$ [Br]) removed oil from O/W emulsion in a short time <20 min with high demulsification efficiency	(Bin Dahbag et al., 2016; Ren et al., 2020)
N_{2224} N $(CN)_2$	Ammonium	Dicyanamide	O/W	–	<90	Steady emulsions were achieved when adding the N_{2224} $N(CN)_2$ ionic liquids due to the presence of surface-active to achieve hydrophilic ionic liquids.	(Bin Dahbag et al., 2016; Ren et al., 2020)
$P_{666,14}$ [N $(CN)_2$	Phosphonium	Dicyanamide	O/W	–	100	$P_{666,14}$ $[N(CN)_2]$ had a great surface-active area and separated the oil from water.	(Bin Dahbag et al., 2016; Ren et al., 2020)
C_8mim Cl	Imidazolium	Chloride	O/W	100–1000	>30	Less hydrophobic cation compared to other ILs cations and achieved lower efficiency.	(Hezave et al., 2013b, a; Hassanshahi et al., 2020)
C_{12}mim Cl	Imidazolium	Chloride	O/W	100–1000	25.2	Less hydrophobicity cation resulted in a low oil recovery rate.	(Hezave et al., 2013b, a; Hassanshahi et al., 2020)

nanoparticle fluid flooding (NFF) have been suggested to be used for improving the oil recovery (Mahmoudi et al., 2019; da Costa et al., 2020). (Purswani and Karpyn, 2019) have examined the mechanism of LSWF in oil/wet carbonate rocks, and they showed that the rise of water/wet causes the increase of oil recovery. Surfactant flooding (SF) has been tested over the previous years, and further green agents have been designed (Deljooei et al., 2021). have prepared a new green surfactant for the oil recovery process, which reveals great wettability alteration and oil recovery abilities. Other oil displacement methods, including filming flooding (FF), has been suggested by (Gao et al., 2019), which shows a high ability to alter the wettability and consequently increase the recovery.

For the surface hydrophobic alteration, it is always favorable to treat organic pollutants in the produced water (Issaoui et al., 2020). have prepared a type of organic clay that demonstrates the high adsorption capacity for bisphenol-A (Wang et al., 2013). have examined gemini and monomer surfactant modified nanoparticles on improving demulsification efficiencies. The results showed that the oil adsorption increases with the modifier's hydrophobicity. The separation process was aimed at a surface ion-exchange or electrostatic interaction among the surfactant and the demulsifier forming a hydrophobic adsorbent surface, which gives a good condition of adsorption (Nguemtchouin et al., 2015; Ghaleh et al., 2020) and enhances the oil recovery by improving the interactions between the demulsifier functional group and the oil (Shen et al., 2018; Han et al., 2019). According to these findings, the surface with unique wetting characteristics is usually dedicated to O/W removal (Beshkar et al., 2020). have produced a hydrophobic/super oleophilic fabric filter for O/W removal with high removal efficiency. The methods and implementations of wettability alteration on the O/W removal deserve more explanation, which gives the most critical impact for its upcoming development.

5. Oil recovery process

Shortly, chemically enhanced oil recovery (EOR) methods will likely perform the primary functions of worldwide crude oil production (Guan et al., 2019). However, until that time, the separation of generated O/W emulsions for the oil recovery process is a crucial advancement in the methodology. As such, steady emulsions can be accomplished by adding the surface-active materials (i.e., surfactant) to the emulsion. For example, in the chemical EOR process (Hjartnes et al., 2019), highlight how the emulsions may have a continuous aqueous phase that includes a mixture of anionic surfactant and materials with high molecular weights (demulsifiers), including hydrolyzed polyacrylamide (HPAM) polymers. Further (Hjartnes et al., 2019), noted that after adding the demulsifier to the emulsion mixture with the application of varying surfactant concentrations, the method ranged between 0.1 to possibly 0.5% by mass. The oil recovery rate improved, although it was reliant upon specific

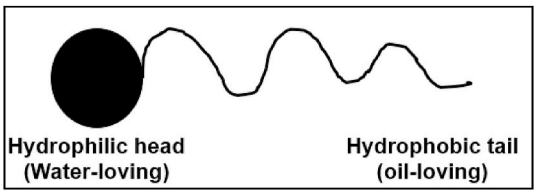

Fig. 2. Structure of surfactant molecule.

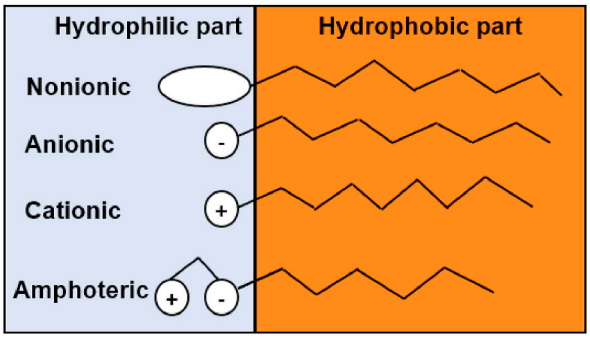

Fig. 3. Surfactant classification (Massarweh and Abushaikha, 2020).

parameters, including the concentration of the demulsifier, the concentration of the surfactant, and process parameters such as pH, salinity, and oil concentration (Hjartnes et al., 2019). The polymer amount was around 0.1% by weight. Other chemicals such as nanoparticles, ionic liquids, and functionalized materials may be present in the enhanced oil recovery chemical mixture as demulsifiers for recovering the oil from O/W emulsions (Elmobarak and Almomani, 2021d). However, in the oil separation method, the surfactant must be favorably solvable in the water phase to dissolve certain oil types. As such, the water phase is an oil-in-water emulsion. Further, the standard method is necessary to create a cost-effective removal of the emulsion with an oil phase including no more than 0.3–0.5 (volume %) water and a water phase including no more than 200 ppm oil (if possible, 100 ppm). (Hirasaki et al., 2011).

6. Mechanisms of oil recovery

The oil recovery mechanism focuses on the electrostatic attraction forces between the oil and applied demulsifier. Overall, the negatively charged oil particles from the O/W emulsion can graft onto the functional groups with positively charged particles on the demulsifier surface via the attractive electrostatic force of the hydrophobic bond (Agista et al., 2018). Most oil removal techniques consist of the

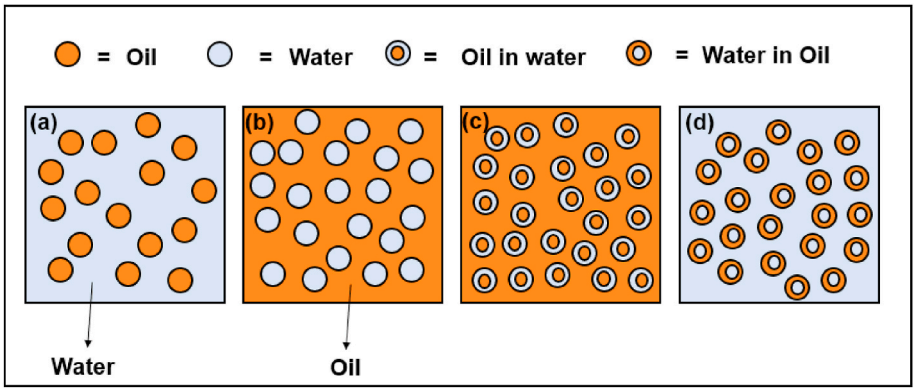

Fig. 1. Emulsion types: (a) oil in water (O/W), (b) water in oil (W/O), (c) multiple emulsion oil in water in oil (O/W/O), (d) multiple emulsion water in oil in water (W/O/W).

dispersion of the demulsifier into the emulsion mixture. The use of magnetic nanoparticle demulsifiers, separately or grafted with other demulsifiers (e.g., polymers and different magnetic nanoparticle types such as silica nanoparticles), introduces a magnetic field, removing NP with adsorbed substances from the emulsion mixture (Esmaeilnezhad et al., 2018). Further, oil separation from O/W emulsion typically relies upon the addition of surface-active compounds that adjust the interfacial properties (such as IFT, mechanical strength, plasticity, and thickness of the interfacial layers). Changing the interfacial properties enhances the oil particle's coalescence and flocculation in the emulsion (He et al., 2015a). Conversely, if the magnetic nanoparticles are added to the emulsion, the demulsifying influence occurs as the remaining particles are covered with interfacial active NP (Liang et al., 2015). Although specific nanoparticles (i.e., iron oxide and iron oxide-based silica NP) have exemplified great efficiency for the oil removal process, the comprehensive mechanism for how the magnetic nanoparticles improve the oil separation rate is yet to be fully realized or thoroughly summarized. Methods for enhancing the oil separation rate through the chemical demulsification process have included IFT decrease, disjoining pressure and movement management, wettability alteration, viscosity management, and demulsification (Yakasai et al., 2020). The methods mentioned above occur because of adsorption, desorption, and oil movement throughout the nanoparticle's pore throat (Ju et al., 2006). Adsorption occurs when the remaining attraction forces are larger than the net repulsion force; otherwise, desorption occurs.

Furthermore, the transportation of the oil particles to the pore throat is pushed by dispersion and convection. Nonetheless, blocking may occur because of the aggregation of oil droplets that are larger than the pore throat (Ju et al., 2006). Research has demonstrated how wettability is a crucial factor for achieving the maximum oil removal rates (Wang et al., 2011). The wettability significantly influences the capillary pressure and porousness — the point at which the oil grafted onto the demulsifier can be considerably enhanced (Bera and Belhaj, 2016). In contrast, the capillary force regulates the IFT between the O/W emulsion and the demulsifier.

Further, decreasing the IFT and adjusting the wettability of the demulsifier correspondingly decreases the capillary pressure and increases the oil removal rate (Elmobarak and Almomani, 2021d). Hence, the existence of the demulsifier aid in reducing the IFT in the absence of the surfactant. Additionally, the demulsifier can enhance the emulsion mixture rheology properties and improve the impact of the surfactant by decreasing the IFT (Munshi et al., 2008). The disjoining pressure mechanism is a new methodology to help interpret the oil removal process and describe the contact between the demulsifier and the oil. Disjoining pressure is the repulsive and attractive force among binary thin films of fluid/solid surfaces (Angle, 2001).

The oil removal methodology is complicated because of a three-phase interaction area (Maghzi et al., 2013). First, the demulsifiers are dissolved into the emulsion to create a wedge-shaped pushed nearer to the oil/demulsifier interaction zone. Second, the required formations in the wedge layer improve the dispersion and grafting of oil droplets onto the demulsifier surface (Wasan et al., 2011). The force generated through a separate molecule is relatively insignificant. However, the overall force of the accumulated demulsifiers is high and reached more than 7.5×10^4 Pa for the nanoparticles when applied during the oil recovery process.

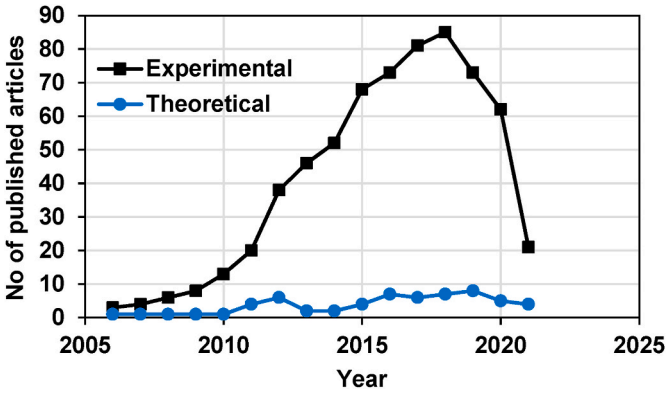

Fig. 5. Research on the application of nanoparticles in the oil recovery process.

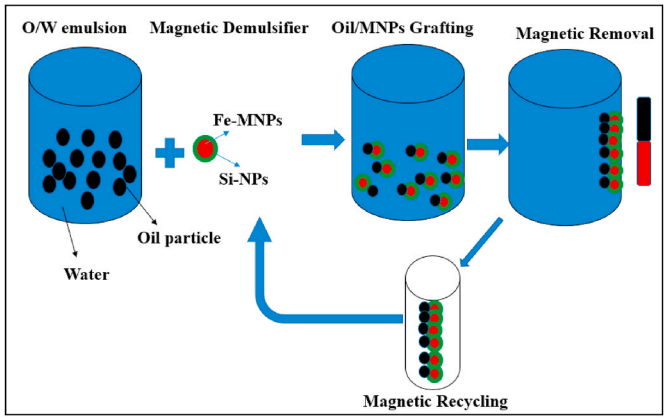

Fig. 6. Application of Fe_3O_4–SiO_2 hybrid nanocomposite in the oil recovery process.

7. Enhanced oil recovery technologies

Presently, there are three main types of technologies for the enhanced oil recovery process: thermal methods, gas methods, and chemical methods (see Table 2) (Kong and Ohadi, 2010; Viebahn et al., 2015).

1) Thermal methods typically dispatch heat into heavy oil reservoirs through several approaches including, steam flooding (SF), cyclic steam stimulation (CSS), and steam-assisted gravity drainage (SAGD). These approaches help to improve the movement capability

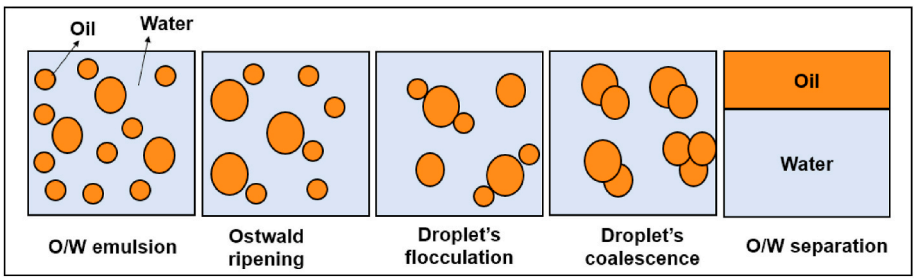

Fig. 4. A representation of the mechanism of the chemical demulsification process (Hassanshahi et al., 2020).

of the heavy oil or asphalt in reservoirs by altering the physical characteristics (i.e., density and viscosity).
2) Gas methods use CH_4, C_3H_8, natural gas (hydrocarbon gases), N_2, or CO_2 (non-hydrocarbon gases) that disperse in oil. The inserted gas can enhance oil recovery by reducing the oil's viscosity and increasing the oil amount.
3) Chemical methods typically include using different chemicals known as demulsifiers, such as polymers, nanoparticles, and ionic liquids to increase the effectiveness of the oil recovery process or the use of surfactants to facilitate the reduction of IFT, which helps to inhibit oil particles from flowing into the reservoir.

To summarize, all the enhanced oil recovery techniques help recover additional oil from reservoirs through several processes, including IFT decrease, wettability alteration, movement management, physical characteristics, and gravity discharge.

8. Chemical demulsification

As an effective and fast demulsification technique, chemical demulsification has been used for several years. Demulsifiers are typically amphipathic composites along with hydrophilic and hydrophobic groups. The oily produced water surface tension can be altered after adding the demulsifier, which encourages the flocculation and aggregation of oil particles by substituting the essential interface active material, thus attaining demulsification (Li et al., 2018; Hou et al., 2019).

For chemical demulsification, greater amounts of alkali, surfactants, and chemicals are used. Demulsifiers are surface-active materials that are efficient at interrupting the impacts of emulsifiers (surfactants) added to the O/W emulsion (Goodarzi and Zendehboudi, 2019). Primarily, surfactants are responsible for stabilizing oil particles, decreasing oil/water interfacial tension, and the zeta potential on the oil particle's surface (Deng et al., 2005). The stages for the chemical demulsification process include the Ostwald ripening (i.e., change in the inhomogeneous structure over time), flocculation, coalescence, and phase separation. The film near the small drops in the O/W emulsion inhibits the water drops from merging to keep the emulsion stable.

Demulsification plays an essential role in separating oil from the water phase, essential in the industrial process (Raya et al., 2020). Crude oil contains pollutants that should be separated because they affect industry equipment, leading to severe problems such as fouling and corrosion. This method can be implemented when demulsifiers are applied. Further, the chemical-based demulsification can cause the coalescence of oil droplets with producing film discharge and improve the surface motion as the gradient is reserved. Additionally, demulsifiers can alter the physical characteristics of the O/W interface. When demulsifiers are inserted into a diluted emulsion with an insignificant concentration, adsorption occurs, which adsorbs the emulsion and locates it onto the surface in droplets (Kokal, 2005). The demulsifier also includes organic molecules and can adsorb the dispersed phase so that the non-polar component will be in the crude oil. In contrast, the polar component remains in the water (Umar et al., 2018).

Demulsifiers have been identified as non-ionic surfactants comprised

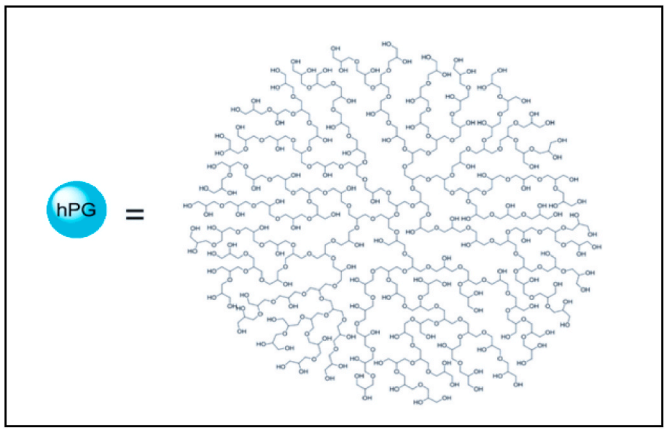

Fig. 8. The structure of a hyperbranched polyglycerol (HPG) polymer (Rabe, 2015).

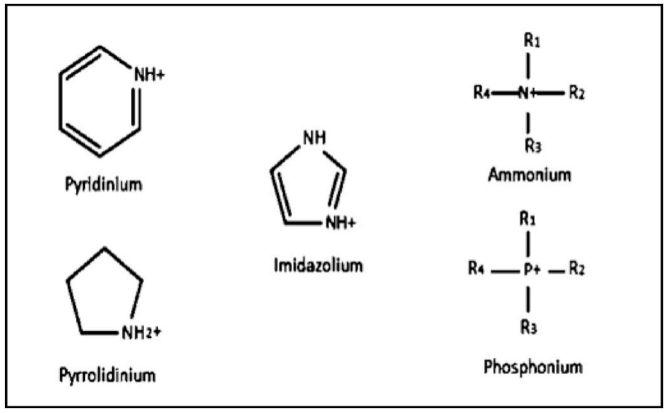

Fig. 9. Common ionic liquids cations (Hassanshahi et al., 2020).

of two individual hydrophobic and hydrophilic components. The hydrophobic group includes alkyl oxypropylenes or alkylphenols, and the hydrophilic group comprises amine groups, oxyethylene, carboxyl, or hydroxyl. Further, several techniques for separating the emulsion include chemical separation, electrical separation, and mechanical separation (Umar et al., 2018). Chemical separation is a common method applied in the industry. The coalescence of O/W emulsions is enhanced, and the protection film is broken using a chemical demulsifier (Martínez-Palou et al., 2013). As such, researchers have endeavored to find a method to speed up the demulsification process efficiency. Numerous techniques were used, such as polymers, nanoparticles, surfactants, and other demulsifier types. According to a study performed by (Al-Sabagh et al., 2011) the separation rate of the (O/W) emulsion improved efficiency when microwave power was utilized. In comparison to the use of chemical non-ionic surfactants, the researchers found that

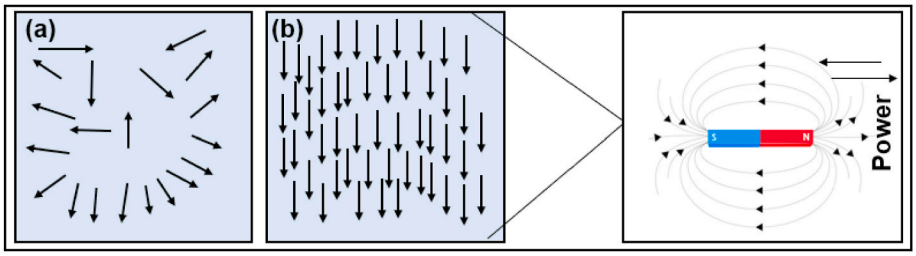

Fig. 7. (a) Superparamagnetic NP dissolved in water demonstrate non-magnetic performance in lack of outside magnetic field (b) Complete alignment of NP when a strong magnetic field is present.

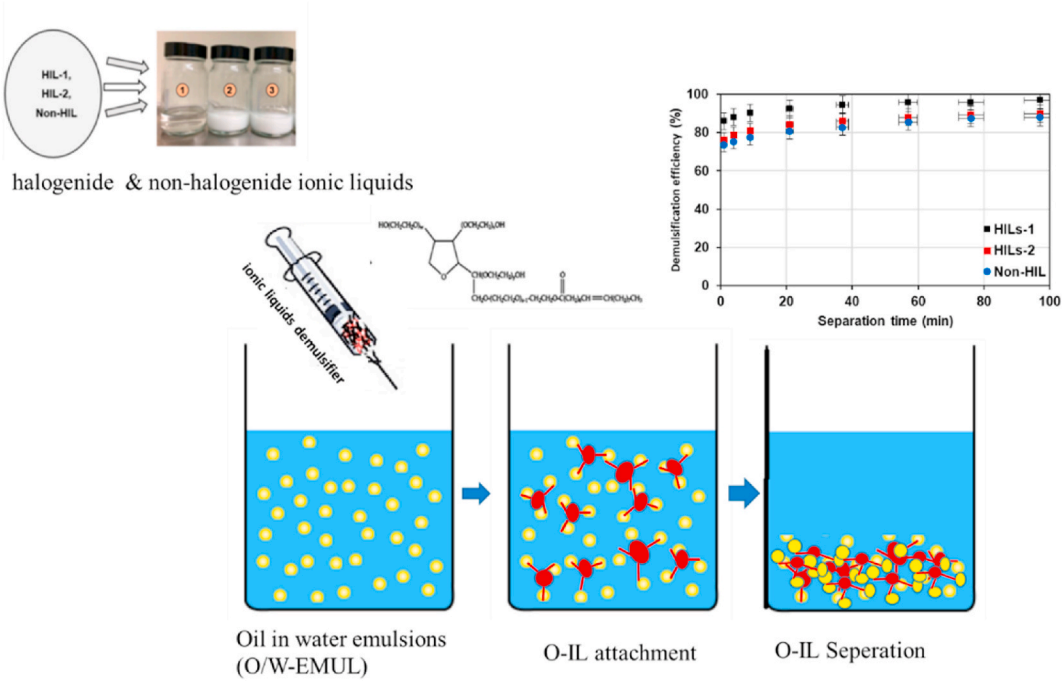

Fig. 10. Application of halogenide (HIL) and nonhalogenide (Non-HIL) ionic liquids for the demulsification process.

the solubility of the surfactant in water declines with the assistance of a saline mixture such as seawater (Al-Sabagh et al., 2011). Conversely, the use of polymers grafted with magnetic nanoparticles was encouraging, as exemplified by (Ali et al., 2015) using Janus magnetic submicronic molecules or P (MMAAA-DVB)/Fe_3O_4. The results demonstrated a high coalescence rate with oil drops settling throughout the magnetism of the external magnetic field. The polymers are reusable, which helps to decrease the overall cost (Ali et al., 2015).

The influential parameters (e.g., oil concentration, HLB, pH, surfactant concentration, salinity, and zeta potential) require further study and consideration to improve the demulsification efficiency. For example, for the oil concentration, the lower concentration it has, the higher the separating rate for the emulsion. Thus, the higher oil content becomes difficult for the demulsifier to disperse in the crude oil. Additionally, an increase in the amount of HLB, surfactant concentration, zeta potential, and salinity demonstrate a decrease in the separation efficiency of this process. However, the higher surfactant amount acts as a steading agent to protect the demulsification of crude oil, which produces a dense film that affects the dispersibility of demulsifiers in the emulsion (Fan et al., 2009; Raya et al., 2020). Fig. 4 illustrates the mechanism of the chemical demulsification process.

8.1. Application of magnetic nanoparticles in the oil recovery processes

Due to the continual increase in global energy demand, innovative technology for improving oil recovery requirements needs to be further developed (Kong and Ohadi, 2010). Developing innovative hydrocarbon supplies is complicated, and the typical oil field has 60–70% non-generated hydrocarbon (Li, 2016). The application of NP in the oil recovery process has a variety of advantages, including (1) high stability as the surface force is more controlling than gravity, (2) the shape and size of the NP can be easily improved using the industrial method with great elasticity, (3) the chemical characteristic of the NP surface can be altered to hydrophobic or hydrophilic, and (4) the most commonly used NP in the oil recovery process is iron oxide and silica NP (99.8% silicon dioxide) which are environmentally friendly materials (Miranda et al., 2012). As such, the three most popular types of NP used in the enhanced oil recovery process are nanofluid, nanoemulsion, and nanofoam. First, nanofluid is a fluid that includes diffuse NP and produces a colloidal suspension. Second, nanoemulsion is a biphasic distribution of two non-miscible liquids, either water in oil or oil in water particles, steadied by the NP — the latter of which is a Pickering emulsion. Third, nanofoam is nanoparticle-steadied gas bubbles in a liquid. The three primary types of NP are grafted NP synergized with surfactants. The most dominant nanoparticles are silica-based of which the surface hydroxyl amount can be altered to make each either hydrophobic or hydrophilic, which results in oil in water and water in oil emulsions, respectively. Experimental tests on enhanced oil recovery using NP have been previously conducted (Cassidy et al., 2013). NP, including graphene, carbon nanotubes (CNT), metallic and metal oxides, have exhibited favorable findings (Nazari Moghaddam et al., 2015) by improving the oil recovery process.

The application of nanoparticles in the oil recovery method can be developed for upstream and downstream (petroleum industry) in discovery, drilling, generation, oil production, and refinery methods (Guo et al., 2017, 2018). Nanoparticles offer a broad field of substitutes for methods and materials in the petroleum industry. Further, the amount of research on the use of nanoparticles (i.e., nanotechnology) within the oil industry has steadily increased. Fig. 5 presents the number of technical papers published in this area of study, indicating many studies, although the petroleum industry is experiencing a downtime. Fig. 5 shows a review of crucial research with the use of nanoparticles in the oil industry.

8.1.1. Characteristics of the nanoparticles

Magnetic nanoparticles (MNP) are a promising material that provides fast improvements and a remarkable ability to remove oil from emulsions. As a result, MNP is commonly used in several fields of advanced science, including thermometry (He et al., 2015b; Zhong et al., 2017) catalysis (Baig and Varma, 2013) information storage (Zhang et al., 2010) environmental preservation (Mohammed et al., 2017), and solar power production (Kovalenko et al., 2016). Typically, MNP is created from a magnetic core made from nickel, cobalt, iron, oxides, and an active-group shell layer. The superparamagnetic or ferromagnetism via magnetic core is conducive for obtaining movement in a specific direction and magnetic production heating below the impact of various magnetic domains. Further, the active groups combined on the shell

layer can be coupled with specified particles, thus grafting. Consequently, the grafted magnetic nanoparticles have both properties of the MNP and shell-layer nanoparticles including surface impact, magnetization impact, magneto-mechanical impact, and magnetic induction heating.

8.1.2. Most common nanoparticles for oil recovery application

Silica-based nanoparticles are frequently examined for their use in enhanced oil recovery. They can be generated, have well-identified chemical and physical characteristics, and obtain various properties, including hydrophobicity and hydrophilicity (Miranda et al., 2012). Moreover, silica-based NPs are powerful non-harmful inorganic substances (Hendraningrat, 2015) and have a lower production cost than other nanoparticles (Metin et al., 2012). Several silica NP types have been prepared. They are classified into three categories depending on their wettability performance (Ju et al., 2002): lipophobic and hydrophilic polysilicon (LHP), hydrophobic and lipophilic polysilicon (HLP), and neutral-wet polysilicon (NWP). Silica-based NP can alter the emulsion system wettability when adsorbed. Additionally, silica NP has a high thermal steadiness without the thermal unsteadiness for comparatively superior-temperature uses (Keykhosravi and Simjoo, 2019) as observed using x-ray diffraction (XRD), infrared spectroscopy (IR), and scanning electron microscopic (SEM) analysis(Ju et al., 2006). conducted investigational and theoretical research on using hydrophilic silica nanoparticles for the enhanced oil recovery process. The results indicated that by adding 2.0–3.0% silica NP, the nanoparticles could be adsorbed and change the wettability of the O/W system and enhance the oil recovery (Ju et al., 2006). (Onyekonwu and Ogolo, 2010) presented research on silica nanoparticles dissolved in ethanol, water, and alcohol fluids. The produced silica nanoparticles dissolved in the ethanol changed the wettability from water-wet to oil-wet and acted as surfactants by decreasing the IFT between the O/W phases. Comparably (Hendraningrat et al., 2013b), examined the impact of silica nanoparticles by applying different doses of NP (0.01 to more than 0.1 wt%) dissolved in brine (3 wt% of NaCl). The research of (Hendraningrat et al., 2013b) demonstrated how the contact angle declines when the NP amount rises, though the greater amount enhances the efficiency of the oil recovery process. Moreover, the silica nanoparticles were applied by (Shahrabadi et al., 2012) for the oil recovery from heavy crude O/W emulsions. Silica nanoparticles dissolved in brine in a carbonate core sample increased the recovery by 39%–61% (Jafarnezhad et al., 2017). also examined was the integration of silica nanoparticles with a polymer for enhanced oil recovery (Maghzi et al., 2011). dissolved silica nanoparticles into a PAM polymer mixture (hyperbranched polymer) in a glass micromodel to test the polyacrylamide emulsion rheology properties when silica nanoparticles are added to the emulsion. By adding 0.1 wt% of silica NP to the emulsion, the overall viscosity of the mixture was enhanced, which resulted in additional oil recovery of more than 10% (Maghzi et al., 2011). (Sharma et al., 2015) tested the use of silica NP dissolved in a surfactant and polymer solution for chemically enhanced oil recovery. It was observed that the silica NP could lessen and steady the IFT for the emulsion, resulting in 21% additional recovery in comparison to the surfactant-polymer demulsifiers (Sharma et al., 2015). Further, researchers also noted that the efficiency of the polymers and surfactant-polymer demulsifiers decreased when applying a high temperature to the emulsion system (Sharma et al., 2016; Sharma and Sangwai, 2017). In contrast, the emulsion mixture exhibited a stable performance at higher temperatures using nanoparticles. As such, the silica NP provides a reliable potential solution for high-temperature chemical enhanced oil recovery processes (Sharma et al., 2016; Sharma and Sangwai, 2017). More recently (Kim et al., 2016), prepared a stable decane/brine solution with a small silica NP. The authors (Kim et al., 2016) demonstrated how a larger NP was preferred with a low NP dosage, while a smaller NP was favored with a high NP dosage. Given that, Silica NP is a highly cost-effective and environmentally friendly nanoparticle. However, the threat of dry silica NP must be evaluated because it may be hazardous to people when directly inhaled (Joonaki and Ghanaatian, 2014). Research by (Corredor et al., 2019) exemplified an excellent oil recovery rate ($R_{oil} < 90\%$) achieved by applying a high oil concentration ($C_{oil} < 2000$ mg/L) with the Fe_3O_4 magnetic NP grafted with silica nanoparticles (doses as low as 10 mg/L). The developed magnetic NP exhibited an excellent oil recovery, consistent steadiness, and high magnetization values (between 46.1 and 80.2 emu/g). Adding a 5, 8, 10, and 15 nm silica layer on the Fe_3O_4 magnetic NP surface preserved them from oxidation conditions, expanded their service life, and obtained a high oil separation (96.3%) as noted by (Elmobarak and Almomani, 2021d). Further, magnetite (Fe_3O_4) MNP can be applied separately in the oil recovery from O/W emulsions, as outlined in our previous study (Elmobarak and Almomani, 2021b). The Fe_3O_4 achieved an oil removal of $\geq$98% for C_{oil} in the range between 200 and 660 mg/L (Elmobarak and Almomani, 2021b). More than 98.6% of the $\%R_{oil}$ was performed for the C_{oil} in the range between 0 and 800 mg/L using only 10 mg/L of Fe_3O_4 MNP (Elmobarak and Almomani, 2021b). Similarly, a smaller dose of Fe_3O_4 (5 mg/L) recovered more than 55.6% of the oil. See Table 3 for a summary of the recent experimental research on the application of (some) nanoparticles, including iron oxide and silica nanoparticles in the oil recovery process. Also, the mechanism of the demulsification process using Fe_3O_4–SiO_2 hybrid nanocomposite in the oil recovery process was illustrated in Fig. 6.

8.1.3. Parameters affecting the application of nanoparticles in oil recovery

8.1.3.1. Nanoparticle size. The nanoparticle size dramatically affects the demulsification process and oil production rates. A smaller NP size will provide a greater particle force (density) and a smaller contact angle between the oil and water surface for a comparable mass. However, a greater particle force significantly increases the oil droplets' coalescence. Thus, it enhances the oil recovery (Kondiparty et al., 2011), while smaller NP will disperse more quickly than larger particle molecules for fewer hydrophilic surfaces. In addition (McElfresh et al., 2012), showed that smaller molecules could cause a more significant charge density and superior electrostatic repulsion, presuming the stability of the nanoparticle. Moreover (Hendraningrat et al., 2013c), noted that smaller nanoparticle sizes had been observed to significantly improve oil recovery and enhance the movement efficiency of the nanoparticles inside the emulsion. Previously conducted tests determined that tinier particles would cause a greater final oil production rate (El-Diasty and Aly, 2015). Further (Kondiparty et al., 2011), highlighted how reducing the diameter of the nanoparticles from 30 nm to 18.5 nm quadrupled the efficiency of the oil recovery. As such, small particles are often better for achieving high oil recovery (Hendraningrat, 2015). However, it is essential to highlight that great surface energy can increase the accumulation and adsorption of the tiny nanoparticles on the surface, which subsequently influences the emulsion stability. Additionally, the size of the NP affects the surface functionalization (coating) method with other materials (demulsifiers). Thus, it is believed that there would be an optimum value for the size of these nanoparticles.

8.1.3.2. Nanoparticle concentration. The nanoparticle concentration is one of the most critical parameters that define the oil recovery method (Chengara et al., 2004). exemplified how the oil recovery improves by raising the NP concentration, enhancing the repulsion forces inside the emulsion. Applying high NP amounts will also enhance the oil recovery efficiency because of the improvement in the NP dispersion in the emulsion (El-Diasty and Aly, 2015). Further, the IFT between both phases (oil and water) can be considerably reduced by enhancing the concentration of the NP (Hendraningrat et al., 2013a). A high NP concentration also leads to a greater wettability alteration impact. Thus, a greater concentration of NP is preferable to achieve a greater oil recovery rate.

However, there is a maximum limit to the NP volume. Going over a

specified limit with the nanoparticles will likely affect the emulsion stability and negatively impact the demulsification process. On the other hand, the accumulated NP will gather in the emulsion when the nanoparticles are very high and decrease the oil recovery effectiveness (Hendraningrat, 2015). (Hendraningrat et al., 2013a) described how the oil recovery was reduced by roughly 2% with silica NP with an amount exceeding 0.5 wt%. As such, an ideal amount of NP is essential to obtain the highest production of oil. However, this amount differs based on the nanoparticle type, emulsion type, and preparation conditions.

8.1.3.3. Salinity. The salinity of the O/W emulsion has a substantial impact on the nanoparticle dispersion stability. A high salinity value lowers the nanoparticle's zeta potential values, resulting in simple accumulation (i.e., aggregation) (McElfresh et al., 2012). As the surface of the emulsion is charged, it is assumed that the magnetism and collision will not occur for the particle/surface but can occur for the particle/particle (Urian et al., 2021). As such, in a high salinity condition, functionalization of the NP is critical for preserving steadiness which can be achieved by surface grafting, ionic control with a surfactant, or an integration of both (El-Diasty and Aly, 2015). (Worthen et al., 2016) exemplified the steadying of nanoparticles by attaching polymers with a low molecular weight to the NP surface in a high-salinity condition. The study noted that with high salinity conditions, the NP stabilization was enhanced (Worthen et al., 2016).

Conversely (Hendraningrat, 2015), demonstrated how adding NP with a high salinity could change the wettability to be further water-wet. At higher salinity conditions, the adsorption of the nanoparticles is enhanced because of the rise in chemical exchanges (Zhang et al., 2015). Comparably (Kanj et al., 2009), determined that improving the emulsion stability did not prevent the transfer of nanoparticles, but it did enhance the adsorption on the nanoparticle's surface. Given that, improving the NP adsorption helps to increase the oil production rates. However, the NP stability will decrease in high salinity conditions. Thus, the correct salinity range and surface grafting are essential characteristics that need to be studied in greater detail to avoid the aggregation of nanoparticles.

8.1.3.4. Wettability. Wettability is a vital component of the NP dispersion as it influences the dispersion and movement of the NP in the emulsion (Fletcher and Davis, 2010). As such, improving the wettability of the emulsion helps improve the oil production rates and vice versa (Garcia-Olvera and Alvarado, 2016). Research conducted by (Agbalaka et al., 2008) exemplified how water wetness is beneficial for more effective oil recovery. However, in particular situations, an oil/wet emulsion (Saha et al., 2018) and neutral wettability (Agbalaka et al., 2008) provide greater oil generation. Enhanced oil recovery process using nanoparticles (nano-EOR) defines the wettability alteration scale. An investigational report using silica nanoparticles found that the maximum oil generation was obtained from an intermediary/wet system (Hendraningrat et al., 2013a). In an intermediary/wet system, oil and water have unstable conditions, which lowers the chance of oil removal in the emulsion (Hendraningrat et al., 2013a). Moreover (Li, 2016), asserted that wettability influences NP adsorption. Water/wet and neutral/wet emulsions have a greater NP adsorption than the oil/wet emulsion mediums. As such, the impact of the nanoparticles on the oil/wet emulsions is reduced. Further examination is necessary to understand the familiar and undetermined factors that can influence the use of nanoparticles in oil production methods. Gaining more knowledge about the approach and influential factors is key to determining practical applications for NP in the enhanced oil recovery process.

8.1.3.5. Surface coating of nanoparticles. The greater physical and chemical characteristics exhibited by the MNP partially rely on surface functionalization, and surface grafting plays a crucial role in implementing the MNP in oil field applications. Several substances can be applied for surface functionalization of the MNP, including amine, polyvinylpyrrolidone (PVP), tetramethylammonium hydroxide (TMAOH), oleic acid, polymers, surfactants, and inorganic substances (Xin et al., 2012; Sodipo and Aziz, 2016). Various methods were applied to prepare surface-grafted magnetic nanoparticles, including co-precipitation (Gnanaprakash et al., 2007), sol-gel technique (Niederberger, 2007), hydrothermal technique (Li et al., 2014), electrochemical (Ramimoghadam et al., 2014), vapor phase procedure, (Wang et al., 2015b), and thermal decomposition (Sharma and Jeevanandam, 2013). Surface functionalization improves the stability of the magnetic nanoparticles and enhances their dispersibility in oil/water emulsion mixtures. Surface functionalization also helps to enhance the surface activity of the MNP and develop the physical and chemical properties of the MNP(Zhu et al., 2018). Using a specified coating on the MNP surface fulfills the requirement for magnetic nanoparticles that have been utilized in oil field settings, including (Yu et al., 2014): (i) the MNP should remain steady for an extended time without aggregate production when separately spread in the emulsion solution, (ii) the MNP have to transference through the emulsion for a long space with slight retention, and (iii) the MNP should only be adsorbed at predictable spots such as adsorbing at the oil/water interfaces of the remaining oil. Moreover, the type of nanoparticle, sonication (before and after the addition of a dispersant), and the MNP distribution in the emulsion effect the MNP dispersion in the emulsion mixtures (Khan et al., 2015).

8.1.3.6. Nanoparticle magnetization. Iron oxide (Fe_3O_4 or Fe_2O_3) nanoparticles have been suggested as nanodevices with distinctive magnetic and electric characteristics (Negin et al., 2016). However, there is only a limited amount of research on iron oxides for the enhanced oil recovery process (Haroun et al., 2012). examined numerous metal oxide NP, including NiO, Fe_2O_3, and CuO, on the carbonate nucleus's plugs. The iron oxide nanoparticles' outcome was disappointing as they only achieved a maximum oil recovery of 57%, while other nanoparticles can achieve more than 85% recovery. In contrast, other researchers have had greater success with iron oxide nanoparticles, noting that the NP could achieve an oil recovery efficiency by more than 24% (extra) when dispersed in water (Ogolo et al., 2012). Similarly (Joonaki and Ghanaatian, 2014), observed that Fe_3O_4 or Fe_2O_3 could remove 17% additional oil compared to nanoparticles that included SiO_2 and Al_2O_3, which separated approximately 20% extra oil (Shekhawat et al., 2016). examined the efficiency of magnetite Fe_3O_4 for heavy oil recovery using a magnetic field. The mechanism of magnetic recovery works by applying an external magnet to the oil in water emulsion and by pushing the NP towards the magnet to remove the greatest amount of oil possible.

Magnetic nanoparticles are categorized as either ferromagnetism or paramagnetism, dependent upon impulsive magnetization. The size of the nanoparticles largely influences the magnetic characteristics. When the size of the nanoparticle is under a particular value, it creates a separate magnetic field. Magnetic fields are the zones wherein each magneton in a specified amount of ferromagnetic substance similarly aligns below the impact of the exchange force (Yusoff et al., 2018). As the single magnetic domain nanoparticle diameter is smaller than what the superparamagnetic shows (typically from 3 to 50 nm according to the materials), the coercive force achieves zero, and the NP demonstrates superparamagnetic performance (Akbarzadeh et al., 2012).

The superparamagnetic NP are commonly used MNP, which are primarily produced by thermal impacts. Typically, the super paramagnets magnetization curve demonstrates no hysteresis and varies from ferromagnets. Superparamagnetic NP distributed into the emulsion mixture have exhibited a nanomagnetic performance in the non-existence of an outer magnetic domain (Fig. 7a). When a low magnetic field is introduced, the thermal agitation can partially overcome the movement of the dipole moment alignment near the magnetic field. As the magnetic domain power rises, the superparamagnetic NP will gradually line up. However, when it exceeds a specific value, the

magnetization achieves the saturation condition and aligns the superparamagnetic nanoparticles (Prodanovic et al., 2010), as exemplified in Fig. 7b. The magnetization of superparamagnetic NP, defined by the modified Langevin function, relies on the intensity of the magnetic field (H) and the saturation magnetization of the superparamagnetic NP (M_s) (Pisane et al., 2015; Macnae, 2017):

$$M = M_0 L \frac{(\mu_p H)}{K_B T} + X_a H \quad (1)$$

where $L(x) = coth\ -1/x$ is the Langevin function, x is the Langevin factor, μ_p is the median magnetic moment of every superparamagnetic NP, and x_a is the linear compound of the sensitivity. Thus, superparamagnetic NP can produce inducement domains when exposed to an external magnetic field conducive to releasing their sites and can be achieved remotely.

8.2. Application of hyperbranched polymers in the oil recovery processes

Because of the branched and three-dimensional expanded structure, polymer demulsifiers are beneficial for treating oily wastewater (Zheng et al., 2015). (Le Follotec et al., 2010) examined the correlation between four triblock copolymers' interfacial characteristics, structure, and demulsification behavior. The researchers observed that the polymers with lengthy hydrophobic bonds are unproductive for both the W/O and O/W emulsions (Le Follotec et al., 2010). In contrast, polymers with shorter hydrophobic bonds were operative in the demulsification process (Le Follotec et al., 2010). Furthermore (Wang et al., 2015a), produced 20 polyether copolymers dependent on polyethyleneimine (PEI). It examined the impact of the intermediary size and the ratio between EO/PO on the effectiveness of the demulsification process using the polyether. The findings demonstrated how the demulsification was enhanced by expanding the size of the hydrophobic units of the polymers (Wang et al., 2015a)., Additionally (Pensini et al., 2014), analyzed the interaction between the PEO/PPO (diblock) polyether and asphaltene in the O/W emulsion. The researchers observed that demulsification could be obtained at an extremely small amount (Pensini et al., 2014).

In a comprehensive review by (Abidin et al., 2012), there was some promise that the use of polymers may play an important role in covering the present energy need as the use of polymers in particular enhanced oil recovery fields has exemplified an ability to regenerate up to 20% extra oil from oil content. For the demulsification of O/W emulsions using polymers as demulsifiers, the HPAM polymer is widely used in the oil recovery process. It was noted as effective in enhancing the stability of O/W emulsions. However, it can complicate the water treatment process (Li et al., 2007). also conducted several tests to determine the effect of the adsorbent amount on sorption efficiency. The researchers (Li et al., 2007) further studied the impact of HPAM on O/W interfacial characteristics and the stability of emulsions developed by crude oil. The study (Li et al., 2007) was carried out by measuring the IFT, zeta potential, and emulsion stability (Li et al., 2007). noted that the HPAM could adsorb at the O/W interface between the oil phase (oleic) and water without reducing the IFT. The improvement in the concentration of the HPAM polymers correspondingly improves the zeta potential and emulsion stability. The findings from this research (Li et al., 2007) can assist in choosing surfactant(s) used in O/W emulsions.

Moreover (Li et al., 2005, 2007), conducted investigations on the chemical description of the emulsions formed using paraffinic crude oil comprised of tiny concentrations of asphaltene and low acid numbers known as the chemical description Daqing crude oil, located in Northeastern China. In this process (Li et al., 2005, 2007), hyperbranched demulsifiers polymerized in sodium hydroxide solutions were applied to recover crude oil. As such, the oil recovery was enhanced, but the generated oil was accompanied by strong, steady O/W emulsions (Li et al., 2005, 2007).

Hyperbranched polymers have unique shapes, sizes, and interfacial movements and can change the basic interfacial active materials at the O/W interface, making them promising for O/W separation (Wang et al., 2007). As previously discussed, hyperbranched polymers exhibit a superior demulsification behavior than linear polymers because of the additional branch bonds, greater interfacial activity, better dispersion, and larger amounts of end groups. As such, the demulsification behavior of the hyperbranched polymers is associated with different parameters, including branch chain number, molecular weight, hydrophilic units, and grade of isomerism (Wang et al., 2008). synthesized a hyperbranched polymer, called a "broom molecule" polymer, and observed that it had an innovative dendritic structure that exemplified great demulsification behavior compared to the O/W emulsion (El-Sharaky et al., 2019). developed a star molecule that relied on ((nitrilotris (ethane-2,1-diyl)) tris (oxy)) tris (4-oxobut-2-enoicd) and examined its effectiveness in the demulsification process (El-Sharaky et al., 2019). also observed that the star polymer was more effective than the PEO/PPO-based copolymers for crude O/W emulsion treatment (Bi et al., 2017). prepared benzyl-G3 and octyl-G3 hyperbranched demulsifiers using strict benzyl and elastic octyl as the dominant cores. Both demulsifiers exhibited great demulsification efficiency for the O/W emulsion (Hao et al., 2016). applied triethyl tetramine (TETA) to the central core to produce a hyperbranched demulsifier and obtained a demulsification rate of 96.66% for a diesel/water emulsion using a low demulsifier volume and low temperature in a short amount of time.

Similarly (Yao et al., 2014), produced hyperbranched polymers using methyl acrylate and ethylenediamine. The polymers exemplified a high demulsification efficiency in a diesel O/W emulsion and had very fine oil particles (Yao et al., 2014). Moreover (Zhang et al., 2018), prepared two hyperbranched demulsifiers using an enhanced one-pot technique with ethylenediamine and 1,3-malonediamine as the central cores. The results indicated that the demulsifier with 1,3-malonediamine, as the dominant core, had greater demulsification effectiveness for the diesel/water emulsion than the demulsifier with ethylenediamine as the main core.

Although hyperbranched polymers have been examined for their use in the demulsification process, there are numerous challenges, including the demand for significant amounts, high operational temperature, and sometimes complicated production procedures.(Yao et al., 2014; Bi et al., 2017; You et al., 2018). Furthermore, most polymer demulsifiers are utilized in diesel/water emulsions (Yao et al., 2014; Zhang et al., 2018). There are only a few articles on the treatment of produced O/W emulsions using HPG polymer demulsifiers (Kuang et al., 2020). prepared HPG with 4,4-diamino diphenyl methane as the main core and observed that it could only separate the diesel/water emulsion and required a high temperature (60 °C). Another hyperbranched macromolecular demulsifier was developed and used to separate oil from oily wastewater using a one-pot technique with 1,4-phenylene diamine (PPDA) as the dominant core and ethylenediamine and methyl acrylate as the chain components (Kuang et al., 2020). The results indicated that PPDA could separate the oil using a low demulsifier amount and exemplified a great efficiency in the demulsification process (Kuang et al., 2020). Significantly, PPDA can be used at an ambient temperature. The impact of the demulsifier dosage, settling time, temperature, and other parameters on demulsification efficiency were analytically examined. As such, Table 4 outlines some types of hyperbranched polymers applied in the oil recovery process.

Hyperbranched polyglycerol polymers (HPG) are a type of hyperbranched polymer commonly used in the biomedical industry and can be used for water treatment and oil recovery processes (Zheng et al., 2015). HPG are biodegradable, cost-effective, easy to develop and produce, and have a high oil recovery rate (Chen et al., 2018; Zhang et al., 2018). The structure of the HPG includes hydrophilic and hydrophobic functional groups that help decrease the IFT among the oil and water. Lowering the IFT immediately enhances the flocculation and coalescence of oil particles which subsequently enhances the separation of the two phases

(Kailey et al., 2013; Yao et al., 2014). HPG polymers provide a rapid separation of phases which causes the oil to be quickly separated from the water once the polymer is added to the emulsion mixture. Consequently, this enhances the polymer efficiency for oil recovery within a small amount of time. HPG polymers are green demulsifiers (i.e., environmentally friendly), and their use in the oil recovery process reduces the use and amount of toxic compounds (Fard et al., 2016; Zhu et al., 2017).

Fig. 8 illustrates the structure of the hyperbranched polyglycerol polymer. In our previous work (Elmobarak et al., 2020), the HPG provided great outcomes in the oil recovery process as a green and efficient technology for oil recovery and separation from O/W emulsions.

In the previous work, (Elmobarak et al., 2020), the demulsification method separated the oil from O/W emulsions into bulk oil and water phases. The demulsification process is characterized by four steps: destabilization, aggregation, coalescence, and gravity separation. In our previous research, chemical demulsification was applied with the addition of specified amounts of HPG polymer to the O/W emulsion (Elmobarak et al., 2020). HPG demulsifiers with hydrophobic and hydrophilic features abide by the O/W interface, decrease the IFT, reduce adsorption time, enhance the oil droplet separation rate, and encourage phase separation via improved flocculation and coalescence method (Zhang et al., 2005; Zolfaghari et al., 2016; Elmobarak et al., 2020).

8.3. Application of ionic liquids in the oil recovery processes

Ionic liquids (IL) are a type of demulsifier used in enhanced oil recovery (EOR) methods. The properties of IL are important for the safety and health interests of a variety of industries. Ionic liquids can remain steady even at extreme temperatures (300 °C and above); however, traditional surfactants applied to the emulsion may decompose at high temperatures. Therefore, the IL has distinctive properties in comparison to other demulsifiers (Patel and Lee, 2012). The most commonly studied IL properties are physical properties such as the melting point temperature. For example, the melting point temperatures for the C_2mim BF_4, C_8mim BF_4, N_{6222}mim NTf_2, C_2mim TfO, and C_6mim BF_6 IL were 15 °C, −80 °C, 20 °C, −10.15 °C, and −61 °C, respectively (Hassanshahi et al., 2020). For the application of IL in the oil recovery process, researchers often favor developing and producing room temperature ionic liquids (RTIL), comprised of ions (organic cations and organic or inorganic anions) exhibiting low interactions correspondingly generate a low propensity for crystallization. RTIL is obtainable by preparing organic cations with various materials, including organic anions, acetate, dicyanamide, trifluoromethyl sulfate, inorganic anions, chloride, bromide hexafluorophosphate, and tetrafluoroborate (Berthod et al., 2008). Further, the formation of cations and anions in the emulsion mixture with the presence of a surfactant in the emulsion mixture develops the mechanism of ion exchange which causes oil separation (Berthod et al., 2008). Fig. 9 presents a few popular IL cations containing pyridinium, ammonium, imidazolium, pyrrolidinium, and phosphonium. Table 5 outlines the anions that have been used to prepare ionic liquids.

Certain IL has an amphiphilic formation that attracts the two phases (i.e., oil and water)(Martínez-Palou and Aburto, 2015; Shehzad et al., 2018). The amphiphilic characteristic may be in the anion or cation portion of the IL structure. Thus, according to the position of the amphiphilic structure, ionic liquids can be categorized into anionic or cationic IL (Alves et al., 2017).

(Pillai et al., 2018) examined the impact of various ionic liquids (C_{12}mim BF_4, C_{10}mim BF_4, and C_8mim BF_4) on the demulsification process as well as the IFT decrease of oil in water emulsions at 30 °C. The results indicated that at high concentrations of 12,000 ppm, 5000 ppm, and 2000 ppm for C_8mim BF_4, C_{10}mim BF_4, and C_{12}mim BF_4 IFT values decreased to 14.57 mN/m, 4 mN/m, and 2.1 mN/m for each IL, respectively (Pillai et al., 2018). In comparison to the other ionic liquids, C_{12}mim BF_4 IL demonstrated high performance in the oil recovery process and recovered 32.28% of the oil at an oil concentration of 2000 ppm (Pillai et al., 2018).

8.3.1. Demulsification using ionic liquids

Demulsifiers are surface-active materials used to weaken the emulsion phases for oil separation(Adewunmi and Kamal, 2019; Saad et al., 2019). A surface action of the demulsifier must be greater than that of the surfactants to disrupt the emulsion (Abullah et al., 2016). The surface activity properties of the demulsifier can be assessed through various methods, including electrical conductivity, proton nuclear magnetic resonance (H NMR), and surface tension (Sastry et al., 2012). Moreover, chemical demulsification is created by adding a specified volume of demulsifiers to the emulsion and strongly mixing. After enough time passes for the Ostwald ripening (i.e., changing an inhomogeneous structure over time), flocculation, coalescence, and phase separation occur. Ostwald ripening occurs when the oil (dispersed phase) can disperse in the continuous phase (water phase) to reach coalescence. Flocculation develops when the oil or water particles gather simultaneously in the water phase while their integrity is also protected. Coalescence is an irrevocable process in which oil or water particles marge to produce larger drops (Abdulredha et al., 2020). The separation process occurs following the dispersed phase density (Moradi et al., 2011). Table 6 outlines the recent application of ionic liquids as demulsifiers in the oil recovery process from O/W emulsions. The application of two types of ionic liquids, including halogenide (HIL) and nonhalogenide (Non-HIL) ionic liquids for the demulsification process and their efficiency in oil separation and recovery, was presented Fig. 10.

8.3.2. Ionic liquid demulsification mechanism

The method for the demulsification process using ionic liquids includes two significant phases: diffusion and adsorption. The diffusion method allocates IL particles in the continuous phase before entering the O/W interface (Hezave et al., 2013b, a; Hassanshahi et al., 2020). Conversely, for the adsorption procedure, the dispersed IL particles move over the water phase and extend the O/W interface (Hezave et al., 2013b, a; Hassanshahi et al., 2020). The IL particles later replace the standard surfactants at the interface and alter the viscoelastic characteristics of the interfacial film. This interaction separates the solid film over the O/W drops, which improves the coalescence of the oil particles (dispersed oil particles) (Martínez-Palou and Aburto, 2015; Grenoble and Trabelsi, 2018). The most recent research has noted that IL with hydrophobic surface-active properties can be applied to demulsify W/O emulsions efficiently (Forsyth et al., 2004; Atta et al., 2016). Research conducted by (Hazrati et al., 2018) demonstrated how hydrophobic IL such as Cnmim PF_6 provides a high demulsification efficiency compared to hydrophilic IL such as Cnmim Cl.

To enable the suspension of ionic liquids in the oil phase, organic solvents including methanol and xylene can be used as well as hydrophilic and hydrophobic ionic liquids, correspondingly (Abullah et al., 2016). Additionally, dichloromethane, isopropanol, chloroform, ethanol, toluene, and benzene can be utilized separately or in mixtures to accomplish a similar objective(Oropeza et al., 2016) (Tian et al., 2019). applied C_2mim BF_4 with cyclohexane for oil production from an oily sludge stable emulsion. The results indicated that up to 95% of the overall oil hydrocarbons were recovered using 0.1 mL/g of IL to sludge ratio at 10 min with a shaking rate of 100 rpm (Tian et al., 2019).

9. Challenges and future research

This review provided an overview of the current developments in nanoparticles, hyperbranched polymers, and ionic liquids as chemical demulsifiers for the oil recovery and removal from O/W emulsions. However, the expansion of oil recovery methods using chemical demulsification processes has several challenges. As such, the significant problems for the oil industry are constraints on technology and commercial parts and the deterioration of the public's health and the

environment. Although research has demonstrated that the application of nanoparticles, polymers, and ionic liquid demulsifiers have a high oil recovery rate and improve the demulsification efficiency, some nanoparticle demulsifiers are restricted to laboratory scales and are not yet appropriate for large-scale field application. As such, restrictions that inhibit the use of nanoparticles on a field level include the aggregation of NP in the emulsion under certain conditions of high salinity and high temperatures.

Additionally, the production of consistent nanoparticle mixtures remains an issue. The mechanisms applied for oil recovery and the factors affecting the demulsification process have not been fully clarified. Moreover, a basic understanding of the application of NP in the oil recovery process is constrained by the absence of theoretical and mathematical examinations. The performance of the nanoparticles and many of the models have not been thoroughly considered for chemical interactions.

The hyperbranched polymer demulsifiers also face several challenges for their application in the oil recovery process. Unfortunately, the fast development of nanoparticles for enhanced oil recovery process means that health and safety reports often lag. Furthermore, a crucial problem for expanding NP is the lack of understanding surrounding the impact of several types of nanoparticles on the human body. Given the nano-scale size of nanoparticles, they are liable to be inhaled by humans, potentially causing damage to the lungs.

With these challenges in mind, future research on oil recovery processes using nanoparticles should focus on:

- The production of stable emulsions in more significant amounts for commercial use.
- Numerous NP has exhibited various properties and methods for the oil recovery process. Nonetheless, only a limited number of studies have recommended the use of nanoparticles in emulsion mixtures. Therefore, other uses and superior behavior that can be made feasible by nanoparticle surface functionalization should be examined.
- More experimental schemes for O/W emulsions for oil recovery need to be conducted using magnetic nanoparticles. These schemes will aid in understanding NP in the oil recovery process and nano-EOR processes under experimental conditions.
- Also necessary is optimization research on the factors that affect the application of NP in oil recovery. This exploration will help to develop oil recovery rates and cost-efficiency.
- Investigational studies should be conducted to verify the adsorption and desorption performance through nanoparticle dispersion inside the emulsion mixture, impacting the NP deliverability to the O/W interface.
- Combined research on nanoparticle safety and health should be conducted to avoid detriment to human health and the environment.

Based on a literature review, hyperbranched polymers have not been widely studied in the field of oil removal. This lack of literature may be partly due to the multistep preparation, which requires greater knowledge and the requirement to assess the polymer structure for the oil removal application. However, given that HPG polymers are commonly used in biomedical applications, there is a possibility of using HPG demulsifiers in the oil recovery process from O/W emulsions.

The efficiency of the demulsification process can be improved by choosing suitable ionic liquids and volumes for specified emulsion types to detect the optimum treatment conditions. Thus, while there are benefits to the use of IL, there are a more significant number of constraints that require further investigation, especially for broader use.

10. Conclusion

Different demulsifiers used for the recovery of oil from emulsions were presented. Nanoparticles (NPs) in general and magnetic NPs in specific showed promising replacement for other EOR process technologies to enhance and achieve the highest oil recovery rates. The NPs have a variety of beneficial features including nanoscale size that provides a larger surface area and dispersion throughout the emulsion. Hyperbranched polymers with distinctive three-dimensional structures grafted onto responsive end groups have exemplified an excellent potential in the oil recovery process from O/W emulsions. The polymers exhibit a great core and outside specific areas that can attach with the oil in the emulsion (oil) through broad types of interactions. Polymers can be functionalized with other materials to achieve a high demulsification efficiency with effective regeneration processes. Ionic liquids have become significantly advanced and exemplify high oil recovery rates. However, some limitations require additional research to ensure their suitability for comprehensive implementation. The literature review revealed that the application of functionalized MPNs and hyperbranched polymers were very effective in recovering up to 95% of oil from oil in water emulsions. Small concentrations of NPs can significantly enhance the oil recovery behavior and high demulsification efficiency at room temperature. The NPs can also easily be integrated and functionalized with additional materials (e.g., polymers and surfactants) to improve the oil separation capacity. NPs (organic and inorganic) can be coupled with silica to obtain excellent oil separation efficiency as a results of the decrease in the IFT and dispersion. The concentration, size, and wettability of NPs influence the behavior in the oil recovery. Future research must be focused on upscale the use of NPs in the oil recovery process and highlights differences between lab-scale and field-level applications. Polymers with highly hydrophilic content and big molecular weight are effective demulsifiers and achieved high oil recovery rates due to their higher interfacial activity, higher dispersibility, and the presence of sensitive functional groups. Ionic liquids could be effectively employed for treating petroleum emulsions and achieving high oil recovery (>90%) if the cost is managed.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Open Access funding provided by the Qatar National Library.

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Nomenclature

Abbreviation Name

O/W	Oil in water
NP	Nanoparticles
HP	Hyperbranched Polymers

HPG	Hyperbranched Polyglycerol
W/O/W	Water in oil in water
O/W/O	Oil in water in oil
RSN	Relative solubility number
HLD	Hydrophilic-lipophilic deviation
HLB	Hydrophilic-lipophilic balance
$\%R_{oil}$	Percentage Oil recovery rate
EOR	Enhanced oil recovery
HPAM	Hydrolyzed polyacrylamide
LHP	Hydrophilic polysilicon
HLP	Hydrophobic and lipophilic polysilicon
NWP	Neutral-wet polysilicon
TMAOH	Tetramethylammonium hydroxide
SF	Steam/surfactant flooding
MD	molecule deposition
LSWF	low salinity water flooding
FF	filming flooding
NFF	nanoparticle fluid flooding
CSS	Cyclic steam stimulation
SAGD	Steam-assisted gravity drainage
MNPs	Magnetic nanoparticles
ILs	Ionic liquids
Wt %	Weight%
RTIL	Room-temperature ionic liquids
mg/L	milligram/litter
ppm	part per million
nm	nanometer

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